Spectroscopic Identification of Fractional Rydberg States of Atomic Hydrogen

Randell L. Mills,* Paresh C. Ray, Bala Dhandapani, Jiliang He

ABSTRACT

Extreme ultraviolet (EUV) spectroscopy was recorded on microwave discharges of helium with 2% hydrogen. Novel emission lines were observed with energies of $q \cdot 13.6\,eV$ where $q = 1,2,3,4,6,7,8,9,11,12$ or these lines inelastically scattered by helium atoms wherein $21.2\,eV$ was absorbed in the excitation of $He(1s^2)$ to $He(1s^1 2p^1)$. These lines can be explained as fractional Rydberg states of atomic hydrogen. Novel emission lines were also observed at $44.2\,nm$ and $40.5\,nm$ with energies of $q \cdot 13.6 + \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) X 13.6\,eV$ where $q = 2$ and $n_f = 2,4$ $n_i = \infty$ that corresponded to multipole coupling to give two photon emission from a continuum excited state atom and an atom undergoing a fractional Rydberg state transition. Such transitions would be extremely energetic; so, the width of the 656.2 nm Balmer α line emitted from the plasmas was measured, and the electron temperature T_e was measured from the ratio of the intensity of the *He* 501.6 nm line to that of the *He* 492.2 line. Significant line broadening corresponding to an average hydrogen atom temperature of $180\text{-}210\,eV$ was observed for helium-hydrogen microwave plasmas; whereas, pure hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3\,eV$. Similarly, the average electron temperature for helium-hydrogen plasma was 28,000 K; whereas, the corresponding temperature of helium alone was only 6800 K.

*Randell L. Mills, BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ 08512, USA, 609-490-1090, 609-490-1066 (fax), rmills@blacklightpower.com

I. INTRODUCTION

J. J. Balmer showed in 1885 that the frequencies for some of the lines observed in the emission spectrum of atomic hydrogen could be expressed with a completely empirical relationship. This approach was later extended by J. R. Rydberg, who showed that all of the spectral lines of atomic hydrogen were given by the equation:

$$\bar{\nu} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1}$$

where $R = 109{,}677\ cm^{-1}$, $n_f = 1,2,3,...$, $n_i = 2,3,4,...$, *and* $n_i > n_f$.

Niels Bohr, in 1913, developed a theory for atomic hydrogen that gave the energy levels in agreement with Rydberg's equation. An identical equation, based on a totally different theory for the hydrogen atom, was developed by E. Schrödinger, and independently by W. Heisenberg, in 1926.

$$E_n = -\frac{e^2}{n^2 8\pi\varepsilon_o a_H} = -\frac{13.598\ eV}{n^2} \tag{2a}$$

$$n = 1,2,3,... \tag{2b}$$

where a_H is the Bohr radius for the hydrogen atom ($52.947\ pm$), e is the magnitude of the charge of the electron, and ε_o is the vacuum permittivity.

The excited energy states of atomic hydrogen are given by Eq. (2a) for $n > 1$ in Eq. (2b). The $n = 1$ state is the "ground" state for "pure" photon transitions (the $n = 1$ state can absorb a photon and go to an excited electronic state, but it cannot release a photon and go to a lower-energy electronic state). However, an electron transition from the ground state to a lower-energy state may be possible by a nonradiative energy transfer such as multipole coupling or a resonant collision mechanism. Processes such as hydrogen molecular bond formation that occur without photons and that require collisions are common [1]. Also, some commercial phosphors are based on resonant nonradiative energy transfer involving multipole coupling [2].

We propose that atomic hydrogen may undergo a catalytic reaction with certain atomized elements and ions which singly or multiply ionize

at integer multiples of the potential energy of atomic hydrogen, $m \cdot 27.2\ eV$ wherein m is an integer. The theory was given previously [3-5]. The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, ..., \frac{1}{p}; \quad p \text{ is an integer} \tag{2c}$$

replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n = 1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but a transition between two nonradiative states is possible via a nonradiative energy transfer, say $n = 1$ to $n = 1/2$. In these cases, during the transition the electron couples to another electron transition, electron transfer reaction, or inelastic scattering reaction which can absorb the exact amount of energy that must be removed from the hydrogen atom to cause the transition. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2\ eV$ (i.e. it absorbs $m \cdot 27.2\ eV$ where m is an integer). Certain atoms or ions serve as catalysts which resonantly accept the nonradiative energy transfer from hydrogen atoms and release the energy to the surroundings to affect electronic transitions to fractional quantum energy levels. As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (2a) and (2c).

A number of independent experimental observations lead to the conclusion that atomic hydrogen can exist in fractional quantum states that are at lower energies than the traditional "ground" ($n = 1$) state. Prior related studies that support the possibility of a novel reaction of atomic hydrogen which produces a chemically generated or assisted plasma and produces novel hydride compounds include extreme ultraviolet (EUV) spectroscopy [6-8, 11-13], characteristic emission from catalysis and the hydride ion products [8], lower-energy hydrogen emission [6-8], plasma formation [8, 11-13], Balmer α line broadening [9], anomalous plasma afterglow duration [13], power generation [9-11], and analysis of chemical compounds [14]. Since the second ionization energy of He^+ is an

exact multiple of the potential energy of atomic hydrogen and microwave plasmas may have significant concentrations of He^+ as well as atomic hydrogen, microwave discharges of helium-hydrogen mixtures were studied by extreme ultraviolet (EUV) spectroscopy to search for line emission from transitions to fractional Rydberg states of atomic hydrogen. Since the electronic transitions are very energetic, Balmer α line broadening and an elevated electron temperature were anticipated and was measured.

II. EXPERIMENTAL

A. EUV Spectroscopy

EUV spectroscopy was recorded on hydrogen, helium, and helium-hydrogen (98/2%) microwave discharge plasmas according to the methods given previously [6]. Hydrogen alone, helium alone, and helium-hydrogen (98/2%) gas mixture was flowed through a half inch diameter quartz tube at 20 torr, 1 torr, or 0.1 torr. The gas pressure inside the cell was maintained by flowing the mixture while monitoring the pressure with a 10 torr and 1000 torr MKS Baratron absolute pressure gauge. The tube was fitted with an Opthos coaxial microwave cavity (Evenson cavity). The microwave generator was a Opthos model MPG-4M generator (Frequency: 2450 MHz). The input power to the plasma was set at 85 watts with forced air cooling of the cell. The spectrometer was a normal incidence McPherson 0.2 meter monochromator (Model 302, Seya-Namioka type) equipped with a 1200 lines/mm holographic grating with a platinum coating or a MgF_2 coating in the case of the spectra recorded at 0.1 torr. The wavelength region covered by the monochromator was $2-560\,nm$. The EUV spectrum was recorded with a channel electron multiplier (CEM) at $2500-3000\,V$. The wavelength resolution was about $0.02\,nm$ (FWHM) with an entrance and exit slit width of $50\,\mu m$. The increment was $0.2\,nm$ and the dwell time was $500\,ms$. Novel peak positions were based on a calibration against the known He I and He II lines.

To achieve higher sensitivity at the shorter EUV wavelengths, the light emission from plasmas of helium alone was recorded with a

McPherson 4° grazing incidence EUV spectrometer (Model 248/310G) equipped with a grating having 600 G/mm with a radius of curvature of $\approx 1\,m$. The angle of incidence was 87°. The wavelength region covered by the monochromator was $5-65\,nm$. The wavelength resolution was about $0.04\,nm$ (FWHM) with an entrance and exit slit width of $300\,\mu m$. A channel electron multiplier (CEM) at $2400\,V$ was used to detect the EUV light. The increment was $0.1\,nm$ and the dwell time was $1\,s$.

B. Line broadening and T_e measurements

The width of the 656.2 nm Balmer α line emitted from hydrogen or helium-hydrogen mixture (90/10)% microwave discharge plasmas was measured. The plasma conditions was as described in section A except that the total pressure was 1 torr, and the input power to the plasma was set at 40 W. The plasma emission was fiber-optically coupled through a 220F matching fiber adapter positioned 2 cm from the cell wall to a high resolution visible spectrometer with a resolution of $\pm 0.006\,nm$ over the spectral range $190-860\,nm$. The spectrometer was a Jobin Yvon Horiba 1250 M with 2400 groves/mm ion-etched holographic diffraction grating. The entrance and exit slits were set to $20\,\mu m$. The spectrometer was scanned between $655.5-657\,nm$ using a $0.005\,nm$ step size. The signal was recorded by a PMT with a stand alone high voltage power supply (950 V) and an acquisition controller. The data was obtained in a single accumulation with a 1 second integration time.

T_e was measured on microwave plasmas of helium alone and helium-hydrogen mixtures (90/10%) from the ratio of the intensity of the *He* 501.6 nm (upper quantum level n=3) line to that of the *He* 492.2 nm (n=4) line as described by Griem [15]. In each case, the microwave plasma cell was run under the conditions given in section A, except that the total pressure was 0.1 torr. The visible spectrum was recorded with the normal incidence EUV spectrometer as described section A except that visible spectrum ($400-560\,nm$) of the cell emission was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT (Model R1527P, Hamamatsu) used has a spectral response in the range of $185-680\,nm$ with a peak efficiency at about $400\,nm$. The scan interval was $0.4\,nm$. The inlet and outlet slit were $300\,\mu m$ with a

corresponding wavelength resolution of 2 *nm*. The spectra were repeated five times per experiment and were found to be reproducible within less than 5%.

III. RESULTS AND DISCUSSION

A. EUV Spectroscopy

The EUV emission was recorded at pressures of 20, 1, and 0.1 torr from microwave plasmas of hydrogen, helium, and helium with 2% hydrogen over the wavelength range 2-125 *nm*. In the case of hydrogen, no peaks were observed below 78 *nm*, and no spurious peaks or artifacts due to the grating or the spectrometer were observed. Only known He I and He II peaks were observed in the EUV spectrum of the control helium microwave discharge cell emission.

The EUV spectra (17.5 – 50 *nm*) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) and the helium control (bottom curve) are shown in Figure 1. Ordinary hydrogen has no emission in these regions. Novel peaks were observed at 45.6 *nm*, 37.4 *nm*, and 20.5 *nm* which do not correspond to helium.

The effect of decreasing the pressure from 20 torr to 1 torr was studied. At the 1 torr condition, additional novel peaks were observed in the short wavelength region. The short wavelength EUV spectrum (5 – 65 *nm*) of the control hydrogen microwave cell emission (bottom curve) is shown in Figure 2. No spectrometer artifacts were observed at the short wavelengths. The short wavelength EUV spectrum (5 – 65 *nm*) of the helium-hydrogen mixture (98/2%) microwave cell emission with a pressure of 1 torr (top curve) is also shown in Figure 2. Novel peaks were observed at 14.15 *nm*, 13.03 *nm*, 10.13 *nm*, and 8.29 *nm* which do not correspond to helium. Known He I lines which were used for calibration of the novel peak positions were observed at 58.4 *nm*, 53.7 *nm*, and 52.4 *nm*.

A broad continuum shoulder on the sharp 45.6 *nm* peak was observed at 20 torr as shown in Figure 1. A 44.2 *nm* peak could be resolved at 1 torr as shown in Figure 2. The effect of further decreasing the pressure from 1 torr to 0.1 torr and was studied using the MgF_2 coated grating. At the 0.1 torr condition, additional novel peaks were

observed. The short wavelength EUV spectrum ($2-50\,nm$) of the control hydrogen microwave cell emission (bottom curve) is shown in Figure 3. No spectrometer artifacts were observed at the short wavelengths. The short wavelength EUV spectrum ($2-50\,nm$) of the helium-hydrogen mixture (98/2%) microwave cell emission (top curve) is also shown in Figure 3. Novel peaks were observed at $45.6\,nm$, $13.03\,nm$, $10.13\,nm$, and $7.60\,nm$ which do not correspond to helium, and novel peaks at $44.2\,nm$ and $40.5\,nm$ could be resolved on the sharp $45.6\,nm$ peak. It is also proposed that the $30.4\,nm$ peak shown in Figures 1-3 was not entirely due to the He II transition. In the case of helium-hydrogen mixture, conspicuously absent was the $25.6\,nm$ ($48.3\,eV$) line of He II shown in Figure 1 which implies only a minor He II transition contribution to the $30.4\,nm$ peak.

At 20 torr, the ratio of the Lβ peak to the $91.2\,nm$ peak of the helium-hydrogen plasma was 2; whereas, the ratio of the Lβ peak to the $91.2\,nm$ peak of the control hydrogen plasma was 8 which indicates that the majority of the $91.2\,nm$ peak was due to a transition other than the binding of an electron by a proton. Based on the intensity, it is proposed that the majority of the $91.2\,nm$ peak was due to a novel peak.

The novel peaks fit three empirical relationships. In order of energy, the set comprising the peaks at $91.2\,nm$, $45.6\,nm$, $30.4\,nm$, $13.03\,nm$, $10.13\,nm$, $8.29\,nm$, and $7.60\,nm$ correspond to energies of $q\cdot 13.6\,eV$ where $q=1,2,3,7,9,11,12$. In order of energy, the set comprising the peaks at $37.4\,nm$, $20.5\,nm$, and $14.15\,nm$ correspond to energies of $q\cdot 13.6-21.21\,eV$ where $q=4,6,\,or\,8$. In order of energy, the set comprising the peaks at $44.2\,nm$ and $40.5\,nm$ correspond to energies of $q\cdot 13.6+\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)X13.6\,eV$ where $q=2$ and $n_f=2,4$ $n_i=\infty$. These lines can be explained as electronic transitions to fractional Rydberg states of atomic hydrogen given by Eqs. (2a) and (2c) wherein the catalytic system involves helium ions because the second ionization energy of helium is $54.417\,eV$, which is equivalent to $2\cdot 27.2\,eV$. In this case, the catalysis reaction is

$$54.417\,eV+He^{+}+H[a_H]\rightarrow He^{2+}+e^{-}+H\left[\frac{a_H}{3}\right]+108.8\,eV \qquad (3)$$

$$He^{2+}+e^{-}\rightarrow He^{+}+54.417\,eV \qquad (4)$$

And, the overall reaction is

$$H[a_H] \rightarrow H\left[\frac{a_H}{3}\right] + 54.4\ eV + 54.4\ eV \tag{5}$$

Since the products of the catalysis reaction have binding energies of $m \cdot 27.2\ eV$, they may further serve as catalysts. Thus, further catalytic transitions may occur: $n = \frac{1}{3} \rightarrow \frac{1}{4}$, $\frac{1}{4} \rightarrow \frac{1}{5}$, and so on.

Electronic transitions to Rydberg states given by Eqs. (2a) and (2c) catalyzed by the resonant nonradiative transfer of $m \cdot 27.2\ eV$ would give rise to a series of emission lines of energies $q \cdot 13.6\ eV$ where q is an integer. It is further proposed that the photons that arise from hydrogen transitions may undergo inelastic helium scattering. That is, the catalytic reaction

$$H[a_H] \xrightarrow{He^+} H\left[\frac{a_H}{3}\right] + 54.4\ eV + 54.4\ eV \tag{6}$$

yields two $54.4\ eV$ photons ($22.8\ nm$). When each of these photons strikes $He\,(1s^2)$, $21.2\ eV$ is absorbed in the excitation to $He\,(1s^1 2p^1)$. This leaves a $33.19\ eV$ ($37.4\ nm$) photon peak and a $21.2\ eV$ ($58.4\ nm$) photon from $He\,(1s^1 2p^1)$. Thus, for helium the inelastic scattered peak of $54.4\ eV$ photons from Eq. (3) is given by

$$E = 54.4\ eV - 21.21\ eV = 33.19\ eV\ (37.4\ nm) \tag{7}$$

A novel peak shown in Figures 1 and 2 was observed at $37.4\ nm$. Furthermore, the corresponding intensity of the $58.4\ nm$ shown in Figure 2 was off-scale with 60,000 photons/sec. Thus, the transition $He\,(1s^2) \rightarrow He\,(1s^1 2p^1)$ dominated the inelastic scattering of EUV peaks. The general reaction is

$$photon\,(h\nu) + He\,(1s^2) \rightarrow He\,(1s^1 2p^1) + photon\,(h\nu - 21.21\ eV) \tag{8}$$

Helium ion catalyzes $H[a_H]$ to $H\left[\frac{a_H}{3}\right]$ as shown in Eqs. (3-5). Further reactions may then proceed:

$$H\left[\frac{a_H}{3}\right] + H\left[\frac{a_H}{3}\right] \rightarrow H\left[\frac{a_H}{4}\right] + H\left[\frac{a_H}{2}\right] + 27.2\ eV \tag{9}$$

It is further proposed that hydrogen transitions from continuum excited states may couple to fractional Rydberg transitions of the same multipolarity. The novel emission lines observed at $44.2\ nm$ and $40.5\ nm$ with energies of $q \cdot 13.6 + \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) X 13.6\ eV$ where $q = 2$ and $n_f = 2,4$ $n_i = \infty$ can be explained by multipole coupling of the

transitions to $n = 1/4$ and $n = 1/2$ with the transition from continuum states to $n = 4$ and $n = 2$, respectively, to give two photon emission.

With inelastic helium scattering and multipole coupling, the three empirical series may be combined. The energies for the novel lines in order of energy are $13.6\,eV$, $27.2\,eV$, $40.8\,eV$, $54.4\,eV$, $81.6\,eV$, $95.2\,eV$, $108.8\,eV$, $122.4\,eV$, $149.6\,eV$, and $163.2\,eV$. The corresponding peaks are $91.2\,nm$, $45.6\,nm$ with $44.2\,nm$ and $40.5\,nm$, $30.4\,nm$, $37.4\,nm$, $20.5\,nm$, $13.03\,nm$, $14.15\,nm$, $10.13\,nm$, $8.29\,nm$, and $7.60\,nm$ respectively. Thus, the identified novel lines correspond to energies of $q \cdot 13.6\,eV$ where $q = 1,2,3,4,6,7,8,9,11,12$, these lines inelastically scattered by helium atoms wherein $21.2\,eV$ was absorbed in the excitation of $He\,(1s^2)$ to $He\,(1s^1 2p^1)$, or the two photon emission from a continuum excited state atom and an atom undergoing a fractional Rydberg state transition. There is remarkable agreement between the data and the proposed transitions. All other peaks could be assigned to He I, He II, second order lines, or atomic or molecular hydrogen emission. No known lines of helium or hydrogen explain the $q \cdot 13.6\,eV$ related set of peaks. Given that these spectra are readily repeatable, these peaks may have been overlooked in the past without considering the role of the helium scattering. It is also remarkable that the novel lines are moderately intense based on the low grating efficiency at these short wavelengths.

B. Line broadening and T_r measurements

The method of Videnocic et al. [16] was used to calculate the energetic hydrogen atom densities and energies from the width of the 656.2 nm Balmer α line emitted from the hydrogen and helium-hydrogen mixture (90/10%) microwave plasmas. It was found that helium-hydrogen showed significant broadening corresponding to an average hydrogen atom temperature of $180\text{-}210\,eV$ and an atom density of $5 X 10^{14}\ atoms/cm^3$; whereas, pure hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3\,eV$ and an atom density of only $7 X 10^{13}\ atoms/cm^3$ even though 10 times more hydrogen was present. Similarly, the average electron temperature for helium-hydrogen plasma was 28,000 K; whereas, the corresponding temperature of helium alone was only 6800 K.

IV. CONCLUSION

We report that extreme ultraviolet (EUV) spectroscopy was recorded on microwave discharges of helium with 2% hydrogen. Novel emission lines were observed with energies of $q \cdot 13.6\,eV$ where $q = 1,2,3,4,6,7,8,9,11,12$ or these lines inelastically scattered by helium atoms wherein $21.2\,eV$ was absorbed in the excitation of $He\,(1s^2)$ to $He\,(1s^1 2p^1)$. These lines were identified as transitions to fractional Rydberg states of atomic hydrogen ($n = \frac{1}{p} = \frac{1}{\text{integer}}$ replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states). Novel emission lines were also observed at $44.2\,nm$ and $40.5\,nm$ with energies of $q \cdot 13.6 + \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) X 13.6\,eV$ where $q = 2$ and $n_f = 2,4$ $n_i = \infty$ that corresponded to multipole coupling to give two photon emission from a continuum excited state atom and an atom undergoing a fractional Rydberg state transition.

An average hydrogen atom temperature of $180\text{-}210\,eV$ was observed by line broadening with the presence of helium ions with hydrogen; whereas, pure hydrogen plasmas showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3\,eV$. Similarly, the average electron temperature for helium-hydrogen plasma was 28,000 K; whereas, the corresponding temperature of helium alone was only 6800 K. No electric field was present in our experiments. Thus, the results can not be explained by Stark broadening or acceleration of charged species due to high fields of over $10\,kV/cm$ as proposed by Videnocic et al. [16] to explain excessive broadening observed in glow discharges.

The novel emission lines and extraordinarily elevated temperatures may be explained by a highly energetic catalytic reaction involving a resonant nonradiative energy transfer of $m \cdot 27.2\,eV$ from atomic hydrogen to a catalyst wherein m is an integer. One such atomic catalytic system involves helium ions. The second ionization energy of helium is $54.4\,eV$; thus, the ionization reaction of He^+ to He^{2+} has a net enthalpy of reaction of $54.4\,eV$ which is equivalent to $2 \cdot 27.2\,eV$. Since the products of the

catalysis reaction have binding energies of $m \cdot 27.2\, eV$, they may further serve as catalysts.

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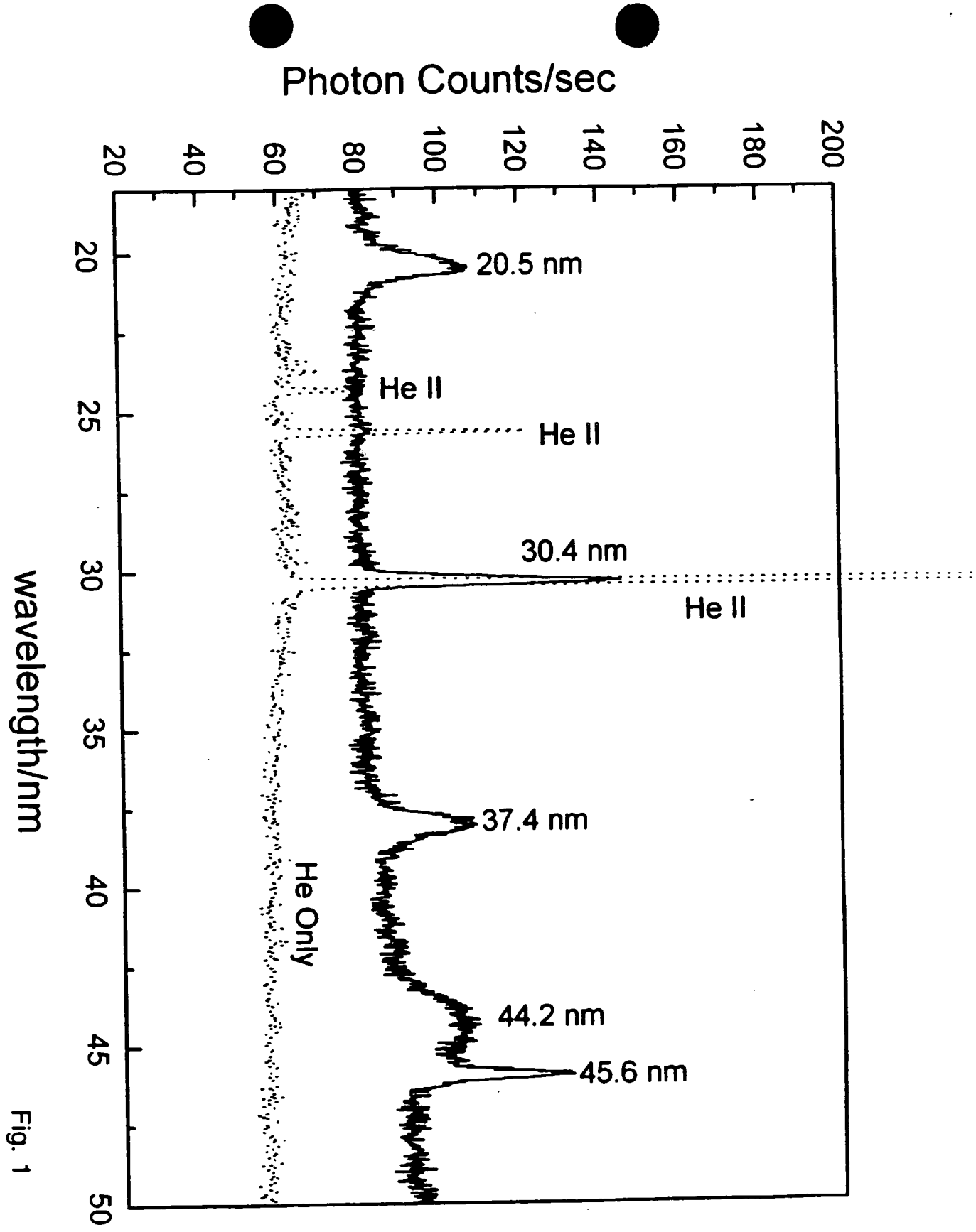
Figure Captions

Figure 1. The EUV spectra ($17.5-50\,nm$) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) recorded at 20 torr with a normal incidence EUV spectrometer and a CEM, and control helium (bottom curve) recorded at 20 torr with a 4° grazing incidence EUV spectrometer and a CEM. Only known He I and He II peaks were observed with the helium control. Reproducible novel emission lines were observed at $45.6\,nm$ and $30.4\,nm$ with energies of $q \cdot 13.6\,eV$ where $q = 2\ or\ 3$ and at $37.4\,nm$ and $20.5\,nm$ with energies of $q \cdot 13.6\,eV$ where $q = 4\ or\ 6$ that were inelastically scattered by helium atoms wherein $21.2\,eV$ ($58.4\,nm$) was absorbed in the excitation of $He(1s^2)$.

Figure 2. The short wavelength EUV spectra ($5-65\,nm$) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) and control hydrogen (bottom curve) recorded at 1 torr with a normal incidence EUV spectrometer and a CEM. No hydrogen emission was observed in this region, and no instrument artifacts were observed. Reproducible novel emission lines were observed at $45.6\,nm$, $30.4\,nm$, $13.03\,nm$, $10.13\,nm$, and $8.29\,nm$ with energies of $q \cdot 13.6\,eV$ where $q = 2,3,7,9,\ or\ 11$ and at $37.4\,nm$, $20.5\,nm$, and $14.15\,nm$ with energies of $q \cdot 13.6\,eV$ where $q = 4,6,\ or\ 8$ that were inelastically scattered by helium atoms wherein $21.2\,eV$ ($58.4\,nm$) was absorbed in the excitation of $He(1s^2)$.

Figure 3. The short wavelength EUV spectra ($2-50\,nm$) of the microwave cell emission of the helium-hydrogen mixture (98/2%) (top curve) and control hydrogen (bottom curve) recorded at 0.1 torr with a normal incidence EUV spectrometer, a MgF_2 coated grating, and a CEM. No hydrogen emission was observed in this region, and no instrument artifacts were observed. Reproducible novel emission lines were observed at $45.6\,nm$, $30.4\,nm$, $13.03\,nm$, $10.13\,nm$, and $7.60\,nm$ with energies of $q \cdot 13.6\,eV$ where $q = 2,3,7,9,12$. Novel emission lines were also observed at $44.2\,nm$ and $40.5\,nm$ with energies of $q \cdot 13.6 + \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) X 13.6\,eV$ where $q = 2$ and $n_f = 2,4$ $n_i = \infty$ that corresponded to multipole coupling to give two photon emission from a continuum excited state atom and an atom undergoing a fractional Rydberg state transition.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200
wavelength/nm
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25
30
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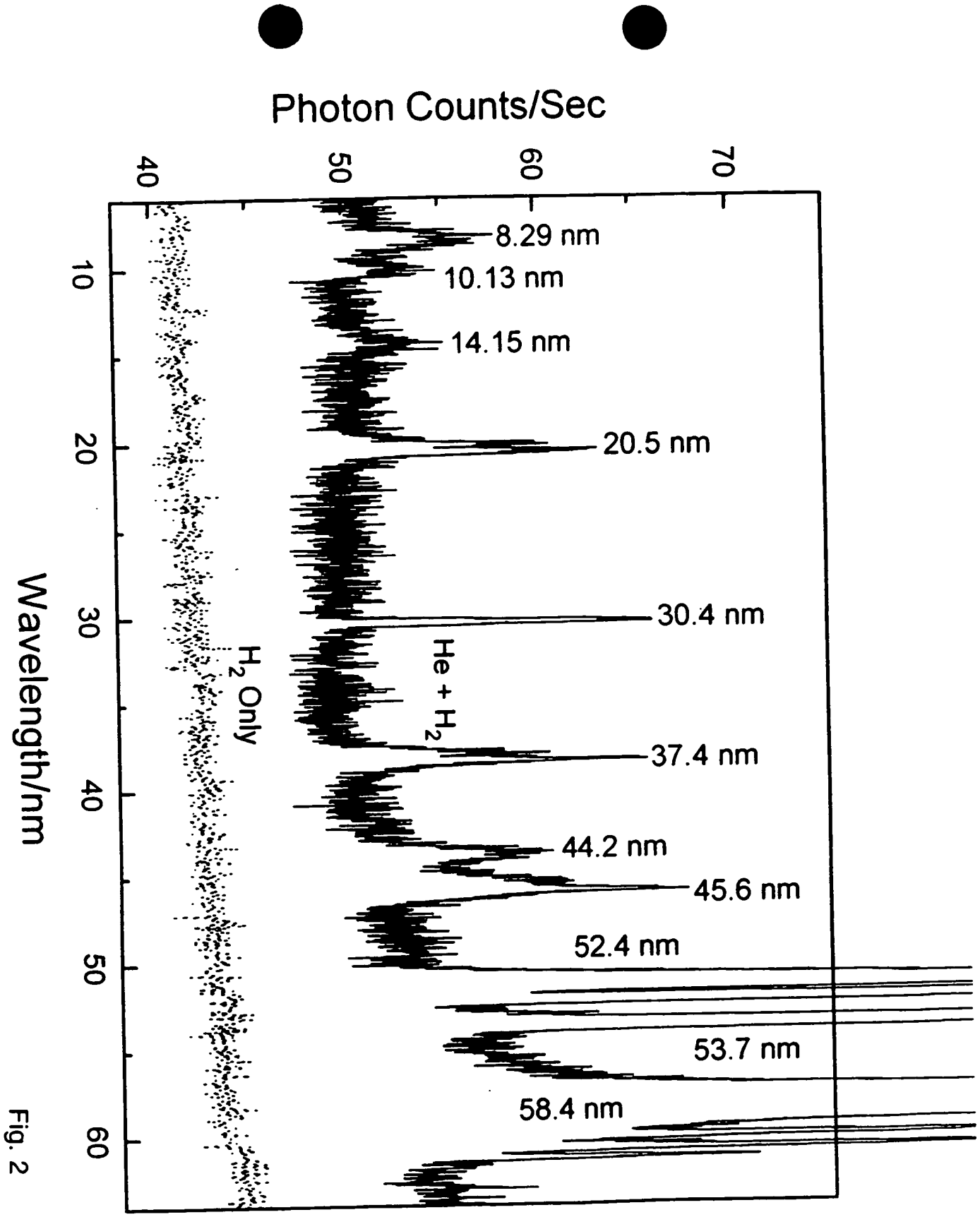
He II
30.4 nm
He II
37.4 nm
He Only
44.2 nm
45.6 nm

Fig. 1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20.5 nm
30.4 nm
37.4 nm
44.2 nm
45.6 nm
52.4 nm
53.7 nm
58.4 nm
H2 Only
He + H2

Fig. 2

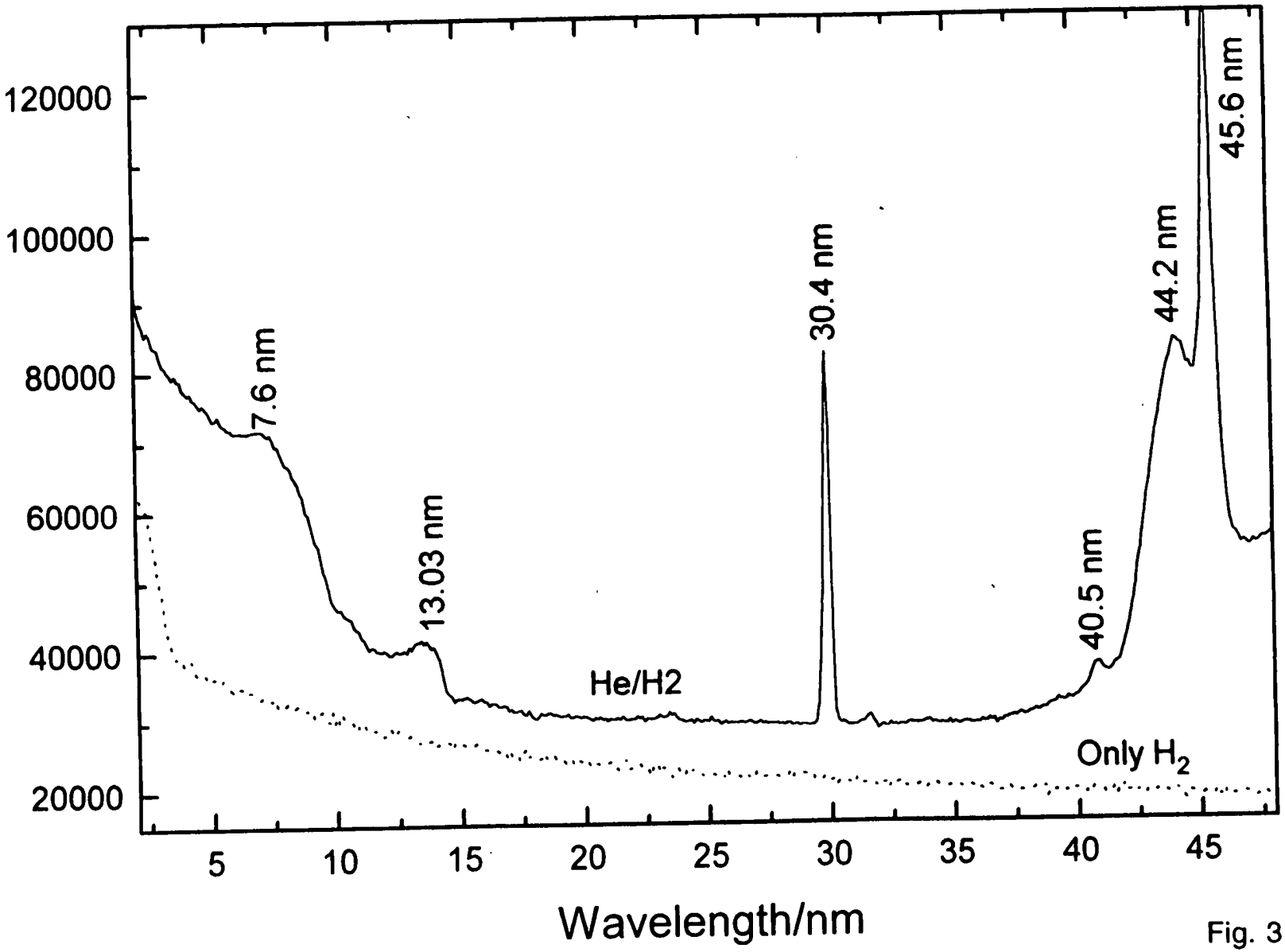
120000
100000
80000
60000
40000
20000
Photon Counts/Sec
5
10
15
20
25
30
35
40
45
Wavelength/nm
7.6 nm
13.03 nm
30.4 nm
40.5 nm
44.2 nm
45.6 nm
He/H2
Only H2

Fig. 3